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A Covalent Triazine Framework, Functionalized with Ir/N-Heterocyclic Carbene Sites, for the Efficient Hydrogenation of CO₂ to Formate

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ABSTRACT: Functionalizing the recently developed porous materials such as porous organic frameworks and coordination polymer networks with active homogeneous catalytic sites would offer new opportunities in the field of heterogeneous catalysis. In this regard, a novel covalent triazine framework functionalized with an Ir(III)-N-heterocyclic carbene complex was synthesized and characterized to have a coordination environment similar to that of its structurally related molecular Ir complex. Because of the strong σ -donating and poor π -accepting characters of N-heterocyclic carbene (NHC) ligand, the heterogenized Ir-NHC complex efficiently catalyzes the hydrogenation of CO₂ to formate with a turnover frequency of up to 16000 h^{-1} and a turnover number of up to 24300; these are the highest values reported to date in heterogeneous catalysis for the hydrogenation of CO, to formate.

1. INTRODUCTION

The need to improve the efficiencies of heterogeneous catalysts is driving the development of heterogenized catalysts across various catalytic processes. Several solid supports, including silica, alumina, zeolite, and others, have been both commercially and academically used to heterogenize various active homogeneous catalysts.¹⁻³ Recently, burgeoning classes of porous materials, such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs) and covalent triazine frameworks (CTFs), have been targeted as catalyst supports because of their potential for incorporating functional organic ligands on the pore surfaces.⁴⁻⁷ Among them, CTFs are particularly interesting owing to their exceptional chemical inertness toward various functional groups, especially in acidic and basic media, and outstanding stability over a broad range of temperatures and pressures.⁸⁻¹² The high surface area with rigid pore structures enable the facile diffusion of substrates and products during catalysis. In addition, the porous properties can be easily tuned within the same array of monomers by changing the synthesis conditions." Moreover, research into shaping the CTFs for industrial applications has also been initiated recently.¹³ Consequently, thus far, organic functional ligands, such as pyridine and 2,2-bipyridine (bpy), have been assembled in CTFs and employed as supports to heterogenize different nitrogen-based transitionmetal complexes.14-22

Despite the fact that pyridine-functionalized CTF catalysts have shown outstanding catalytic efficiencies, their use in catalysis is limited because of the lack of functional and selective sites in CTF materials. To date, in coordination chemistry, apart from pyridine-ligated complexes, a vast number of complexes, particularly with strong electron-donating ligands, have been developed.^{23,24} In many cases, they have shown better catalytic efficiencies than pyridine-ligated complexes.^{25:27} Thus, the design of novel functional CTF materials is essential for the development heterogeneous catalysts. These functionalized CTF materials would offer new opportunities in emerging research fields such as CO₂ hydrogenation, C-H activation, H₂ generation and frustrated Lewis pair chemistry, etc.

In here, we focused on functionalizing CTF-based heterogenized catalyst for the efficient hydrogenation of CO_2 to formate. Although, previously prepared CTFbased half-sandwich Ir-bipyridine complex (bpy-CTF-[IrCp*CI]Cl), reported by us,¹⁴ had shown the best TOF (5300 h⁻¹) among the heterogeneous catalysts, its efficiency is still moderate compared to those of homogeneous catalysts.²⁸⁻³³ Similarly, a sphere-shaped IrCp*attached CTF, which was constructed using a 1:2 ratio of 2,6-pyridinedicarbonitrile and 4,4'-biphenyldicarbonitrile, had also shown very low catalytic activity for this transformation (a maximum TON of 350 was observed).¹³ Scheme 1. Schematic representation of the synthesis of NHC-CTF-based Ir complex Ir-NHC-CTF



^aReagents: (i) ZnCl₂; (ii) [IrCp*Cl₂]₂ and Et₃N.

Theoretical investigations on the hydrogenation of CO₂ demonstrated that the ligands which improve the electron density on central metal ions would enhance the efficiency of this catalytic reaction.³⁴ Consequently, we envisioned that N-heterocyclic carbene (NHC) may be a good choice of ligand for an efficient catalysis because it is well known for its strong σ -donating and poor π accepting characteristics.³⁵⁻³⁷ Accordingly, we focused on employing NHC-functionalized CTF (NHC-CTF) as a solid ligand motif for this catalysis. Utilizing 1,3-bis(5cvanopyridyl)-imidazolium bromide as the monomer (NHC-monomer), a CTF with numerous NHC structural units (NHC-CTF) is accessible (Scheme 1),³⁸ and we postulate that it will allow the coordination of the {IrCp*} unit through N^C coordination bond and form a halfsandwich Ir(III) NHC-complex. Herein, a NHC functionalized CTF was employed to immobilize the halfsandwich Ir(III) complex via post-synthetic metalation using an Ir precursor and a base (Scheme 1). The NHC-CTF-based Ir complex [NHC-CTF-IrCp*Cl]Cl (Ir-NHC-CTF) efficiently converts CO₂ to formate via hydrogenation with highest ever TOF of 16000 h⁻¹ and TON of 24300. Surprisingly, to the best of our knowledge, this is the first example of a NHC-functionalized porous organic framework (POF) employed as a support to heterogenize transition-metal complex through N^C coordination bond.

2. EXPERIMENTAL SECTION

2.1 Materials. All chemicals and reagents were purchased from commercial supplies and used as received unless otherwise mentioned; 1-methyl-1H-imidazole, zinc chloride, anhydrous methanol and chloroform, triethylamine were purchased from Sigma Aldrich. Iridium chloride hydrate, 1,2,3,4,5-pentamethyl cyclopentadiene were purchased from T.C.I. chemicals. 2-bromo-5-cyanopyridine was obtained from AK Scientific Inc. and purified by silica-column chromatography using meth-

ylene chloride. CO_2 (99.99%) and H_2 (99.99%) were purchased from Sinyang gas industries. The Ir precursor, $[IrCp*Cl_2]_2$ was synthesized according to the previously reported procedure.³⁹

2.2 Characterization Techniques. Fourier transform infrared (FT-IR) measurements were carried out on a Nicolet iS 50 (Thermo Fisher Scientific). ¹³C crosspolarization magic-angle spinning solid state nuclear magnetic resonance (¹³C CP-MAS ssNMR) spectroscopic data's were acquired at ambient temperature on 400 MHz Solid state NMR spectrometer (AVANCE III HD. Bruker, Germany) with an external magnetic field of 9.4 T. The operating frequency was 100.66 MHz for ¹³C and the spectra were referenced relative to TMS. The samples were contained in HX CPMAS probe, with 4 mm o.d. Zirconia rotor. Scanning electron microscopy (SEM) and Energy-dispersive spectroscopy (EDS) measurements were performed using JEOL LTD (JAPAN) JEM-7610F operated at an accelerating voltage of 20.0 kV. Xray photoelectron Spectroscopy (XPS) measurements were recorded on a ESCA 2000 (VG microtech) at a pressure of $\sim 3 \times 10^{-9}$ mbar using Al-Ka as the excitation source (hy=1486.6 eV) with concentric hemispherical analyzer. Iridium content in Ir-NHC-CTFs were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) (iCAP-Q, Thermo fisher scientific) using microwave assisted acid digestion system (MARS6, CEM/U.S.A); CTFs (100.0 mg) were digested in a mixture conc. HCl (20.0 mL) and conc. H₂SO₄ (10.0 mL) solution under microwave rays at 210 °C for 60 min (ramp rate = 7 °C/min). N₂ adsorption-desorption measurements were conducted in an automated gas sorption system (Belsorp II mini, BEL Japan, Inc.,) at 77 K; the samples were degassed for 2 h at 200 °C before the measurements. The Barrett-Joyner-Halenda (BJH) method was used for the pore size distribution. Powder X-ray diffraction (PXRD) was measured on a RIGAKU D/Max 2500V using Cu (40 kV, 30 mA) radiation. Solu-

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tion state ¹H and ¹³C NMR were measured on 400 MHz NMR spectrometer (ASCEND III HD, Bruker, Germany). LC-MS measurements were performed on Agilent 6130 Single Quadrupole LC/MS spectrometer. HPLC was measured on Waters Alliance 2695 (Waters Corporation) equipped with a binary pump, an online degasser, an auto sampler, a thermostatically controlled column compartment and a RI detector.

2.3 Synthesis of NHC-monomer. The NHC-monomer was prepared by following the procedure described in 10 the literature.⁴⁰ A mixture of 2-bromo-5-cyanopyridine 11 (20.0 g, 0.109 mmol) and 1-methyl-1H-imidazole (7.47 g, 12 0.091 mmol) were taken in a 50 mL RBF equipped with a 13 vacuum adapter, and alternatively degassed with N₂ and 14 vacuum for three times and closed under vacuum. Heat-15 ed the mixture to 190 °C at a rate of 1 °C /min for 18 h 16 and cooled to room temperature. The resulting black 17 solid was purified in hot methanol, washed with CHCl₂, 18 and dried. Finally, it was recrystallized in methanol to 19 obtain pure NHC-monomer. Yield: 70%. ¹H NMR (400 20 MHz, DMSO-d₆) δ [ppm] = 11.07 (t, J = 1.66 Hz, 1H, 21 NCHN), 9.24 (dd, J = 0.77 Hz and 2.23 Hz, 2H, CH-6py), 22 8.86 (dd, J = 2.23 Hz, and 8.70 Hz, 2H, CH-4py), 8.84 (d, 23 J = 1.66 Hz, 2H, NCHCHN), 8.50 (dd, J = 0.77 Hz, and 24 8.70 Hz, 2H, CH-3py). ¹³C NMR (400 MHz, DMSO-d₆) δ 25 [ppm] = 153.3 (s, CH-6py), 148.5 (s, CH-2py), 145.1 (s, CH-26 4py), 136.3 (s, NCHN), 121.0 (s, NCHCHN), 116.5 (s, C-27 5py), 115.7 (s, C-3py), 111.0 (s, CN). LC/MS (ESI): m/z 28 273.09.

29 2.4 Synthesis of NHC-CTFs. In an Ar filled glove box, 30 the NHC-monomer (1.00 g, 2.83 mmol) and zinc chlo-31 ride (1.92 g, 14.1 mmol) were taken in a 5 mL ampule(s) 32 and closed with vacuum adapters. The ampule(s) were 33 taken out from glove box and sealed under vacuum, and 34 heated to 300 °C or 400 °C in a furnace at a heating rate 35 of 60 °C/h. After 48 h, the furnace was cooled to 200 °C 36 at a cooling rate of 10 °C/h. The resulting monolith was 37 ground well and stirred with 250 mL of water for 3 h and 38 filtered, washed with water (500 mL) and acetone (500 39 mL). The obtained solid was then refluxed in 1M HCl 40 (500 mL) for 12 h, and filtered, washed with 1M HCl 41 (3X100 mL), H₂O (3X100 mL), tetrahydrofuran (3X100 42 mL) and acetone (3X100 mL). To a saturated aqueous 43 NaCl solution (3.0 M), the filtered solids were added and 44 stirred at room temperature for 24 h to metathesis all Br⁻ into Cl⁻ ions. Then, the solid was filtered, washed 45 46 with water (3X500 mL), and acetone (3X100 mL). Final-47 ly, the black powder was dried under vacuum at 200 °C for 10 h. Yield: 0.800 g. 48

2.5 General Procedure for the synthesis of Ir-NHC-CTF. Ir-NHC-CTF was synthesized with three different Ir loadings. In an oven-dried multi neck round bottom flask equipped with a condenser, the NHC-CTF (0.610 g), synthesized at 400 °C, was suspended in a methanol/chloroform mixture under N₂ atmosphere. After 10 min, triethylamine (the amount was varied to 1.5, 4.5 and 6.0 mL, respectively) was added and stirred at room

temperature for 30 minutes. A solution of [IrCp*Cl₂], (the amount was varied to 0.410, 1.00 and 1.50 g, respectively) in a methanol/chloroform mixture was then slowly added and heated under N₂ atmosphere for 24 h. After cooling to room temperature, the black powder was filtered, washed with dichloromethane (3x 250 mL) and acetone (3x 250 mL). Finally, the solid was completely dried under vacuum for 24 h. The dried samples were denoted as Ir_x-NHC-CTF (x denotes the amount (wt%) of Ir loaded in NHC-CTF).

2.6 Synthesis of homogeneous [IrCp*(N^C)Cl]Cl. A mixture of 1-(4-(tert-butyl)pyridin-2-yl)-3-methyl-1Himidazol-3-ium iodide (0.091 g, 0.265 mmol), designated as N^C ligand, (see supporting information for the synthesis) and Ag₂O (0.036 g, 0.159 mmol) in CH₂Cl₂ (15.0 mL) was stirred at room temperature for 5 h under N₂ atmosphere and filtered through celite bed and washed with CH_2Cl_2 (2.0 mL). To the filtrate, [IrCp*Cl_2], (0.105 g, 0.132 mmol) dissolved in CH₂Cl₂ (3.0 mL) was added under N2 atmosphere and stirred for 10 h at room temperature. The resulting white precipitate was filtered, washed with CH₂Cl₂ (3.0 mL) and the filtrate was concentrated under reduced pressure. Finally, it was recrystallized triturated with diethyl ether to afford homogeneous [IrCp*(N^C)Cl]Cl as a yellow solid. Yield = 0.140 g (86%). ¹H NMR (400 MHz, CDCl₂): δ [ppm] = 9.34 (d, J = 1.4 Hz, 1H), 8.79 (d, J = 1.7 Hz, 1H), 8.34 (d, J = 6.2 Hz, 1H), 7.53 (d, J = 10.8 Hz, 1H), 7.33 (dd, J = 6.2, 1.9 Hz, 1H), 4.05 (s, 3H), 1.76 (s, 15H), 1.43 (s, 9H). ¹³C NMR (400 MHz, CDCl₃) δ [ppm] = 168.5, 164.9, 152.8, 148.85, 125.6, 121.1, 119.9, 111.9, 91.8, 37.7, 36.4, 30.5, 9.62. LC/MS (ESI): m/z 578.2 [η⁵-Cp*Ir(N^C)Cl]⁺

2.7 Representative procedure for the hydrogenation of CO₂ to formate

Hydrogenation was carried out in a 100 mL homemade stainless steel reactor equipped with a glass vessel insert. In a typical run, the Ir-NHC-CTF (10.0 mg) was dispersed in a CO₂ saturated aqueous triethylamine solution and kept into the reactor, and tightly closed. After flushing with CO₂, the reactor was initially pressurized with CO_2 and then with H_2 (1:1) to the desired pressure at room temperature and heated at 80-160 °C. The reaction was cooled to room temperature after appropriate time and slowly released the pressure. The concentration of formate was analyzed by HPLC on Aminex HPX-87H column using 5.00 mM H₂SO₄ as an eluent. In the recycling experiments, the catalyst was recovered after each cycles by filtration, washed with water and acetone, and dried under vacuum before next run. By following the similar procedure, the solid was then used for the successive runs.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of NHC-CTF: The synthetic strategy for the preparation of the NHCfunctionalized CTF-based Ir complex (Ir-NHC-CTF) is outlined in Scheme 1. The trimerization of the NHC



Figure 1. Scanning electron microscopy (SEM) image of (a) NHC-CTF and (b) $Ir_{0.68}$ -NHC-CTF; (c) Energy-dispersive spectroscopic (EDS) mapping of the Ir atoms in $Ir_{0.68}$ -NHC-CTF. (d) N_2 adsorption-desorption isotherms of NHC-CTF prepared at 400 °C (red) and $Ir_{0.68}$ -NHC-CTF (blue).

monomer was achieved at two different temperatures (300 and 400 °C) via the ionothermal technique using ZnCl₂ as the catalyst and as a salt melt. The assynthesized CTFs were stable in air and insoluble in nearly all common organic solvents (methanol, ethanol, acetone, acetonitrile, dichloromethane, chloroform, ethyl acetate, dimethylformamide, dimethylsulphoxide, tetrahydrofuran and, diethylether) and water. X-ray powder diffraction analysis revealed that the NHC-CTFs were amorphous in nature (Figure S1). The absence of a nitrile peak representing the monomer at 2236 cm⁻¹ in the FT-IR spectra indicates the complete conversion of nitrile groups (Figure S2). The regional peaks at 115, 131, and 140-165 ppm in the ¹³C CP-MAS ssNMR spectroscopic analysis of NHC-CTFs confirm the presence of pyridine, triazine, and imidazolium units (Figure S₃). In addition, the peak at 137 ppm clearly indicates the presence of carbene sites in NHC-CTFs. N2 adsorptiondesorption measurements revealed that the CTF synthesized at 400 °C showed a type IV adsorption isotherm with a hysteresis behavior (Figure 1d and S4), indicating that the material exhibits both microporous (major) and mesoporous structure (minor) with a total pore volume of 0.38 cm³/g and the Brunauer-Emmett-Teller (BET) surface area of $693 \text{ m}^2/\text{g}$. Conversely, the CTF synthesized at 300 °C showed very low porosity (total pore volume: 0.005 cm³/g and surface area: 2.4 m²/g); the behavior of having low or no porosity in the CTFs synthesized at lower temperature is reported previously.⁴¹ Since the support porosity plays a key role in the diffusion of substrates and products in heterogeneous catalysis, the CTF

synthesized at 400 °C (from here designated simply as NHC-CTF) was subjected to further studies.

3.2 Synthesis and characterization of Ir-NHC-CTF: To synthesize Ir-NHC-CTF, the as prepared NHC-CTF (synthesized at 400 °C) and $[IrCp*Cl_2]_2$ were refluxed in a methanol/chloroform mixture with triethylamine under N₂ atmosphere for 24 h. The amount of Ir loaded on NHC-CTF could be controlled by varying the concentration of $[IrCp*Cl_2]_2$, and three catalysts containing Ir loadings of 0.68, 2.1 and 3.5 wt%) (determined by ICP-OES) were prepared and are designated as Ir_{0.68}-NHC-CTF, Ir_{2.1}-NHC-CTF and Ir_{3.5}-NHC-CTF, respectively. The Ir-NHC-CTFs were stable in air and insoluble in almost all common organic solvents and water. SEM image of Ir_{0.68}-NHC-CTF shows that the original irregular morphology of NHC-CTF remains unchanged during the



Scheme 2. Synthesis of homogeneous [IrCp*(N^C)Cl]Cl.



Figure 2. Deconvoluted XPS C 1s spectra of N^C ligand (a); homogeneous [IrCp*(N^C)Cl]Cl (b); NHC-CTF (c); Ir_{0.68}-NHC-CTF (d).



Figure 3. Deconvoluted XPS N 1s spectra of N^C ligand (a); homogeneous [IrCp*(N^C)Cl]Cl (b); NHC-CTF (c); Ir_{0.68}-NHC-CTF (d).

metalation (Figure 1a and 1b). SEM–EDS mapping showed a homogeneous distribution of the C, N, Cl, and Ir elements in the CTF matrix, evidencing that the metalation has occurred uniformly throughout the framework (Figure 1c and Figure S₅). The formation of IrNHC-CTF was confirmed by ¹³C CP-MAS ssNMR analysis. As shown in Figure S6, compared to the ¹³C CP-MAS ssNMR of NHC-CTF, the intensity of aromatic carbons in the region of 90-145 ppm were increased and a new peak at the aliphatic regions (~10 ppm) was observed.

This new peak is assignable to the methyl carbon of the Cp* unit,⁴² and the increased intensity at the aromatic region is attributed to the overlapped signals of aromatic carbons of NHC-CTF with the aromatic carbons of Cp*. This result clearly indicates the presence of Cp* unit in the Ir_{3.5}-NHC-CTF and thus confirms the coordination of Ir precursor with NHC-CTF support. Finally, the porous properties of Ir_{0.68}-NHC-CTF were realized by N₂ adsorption-desorption analysis performed at 77 K (Figure 1d and S7). The results revealed that Ir_{0.68}-NHC-CTF exhibit a type IV isotherm with hysteresis behavior, suggesting that Ir-NHC-CTFs still exhibit both as microporous and mesoporous material. However, the surface areas and total pore volumes were decreased according to the metal loading amount This indicates that the {IrCp*Cl₂} units partially occupied the pores of NHC-CTF and reduced the accessible pore volumes of CTF. Notably, Ir-NHC-CTF is still a porous material and might facilitate the diffusion of small molecules such as CO_2 , H_2 , H_2O , and formic acid through its pores.

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3.3 Synthesis and characterization of homogeneous [IrCp*(N^C)Cl]Cl: To understand the iridium interaction with NHC-CTF support, a structurally related new homogeneous iridium complex, [IrCp*(N^C)Cl]Cl (inset in Scheme 1), was synthesized as a reference complex. The synthetic scheme for the preparation of homogeneous [IrCp*(N^C)Cl]Cl was outlined in Scheme 2. The N^C ligand was prepared through an additionelimination reaction of 4-tert-butylpyridyl-2-chloride with sodium salt of imidazole, followed by Nmethylation of imidazole ring using methyl iodide. The as prepared N^C ligand was treated with carbene transfer reagent (Ag₂O), followed by reaction with [IrCp*Cl₂]₂ yield the water-stable yellowish orange to [IrCp*(N^C)Cl]Cl in excellent yield. Absence of the peak at 11.33 ppm, which corresponds to NCHN imidazolium proton, and downfield shift of aromatic protons compared to those of N^C ligand in 'H NMR spectrum of [IrCp*(N^C)Cl]Cl indicates that the electron density from the N^C ligand was donated to the iridium metal center. In addition, the lack of characteristic set of two distinct peaks for the 4-tert-butyl-pyridine ring confirms the loss of symmetry and formation of a chelate. The formation of [IrCp*(N^C)Cl]Cl was also evidenced by spectrum through the presence of $[\eta^5$ mass $Cp^*Ir(N^C)Cl]^+$ ion (m/z= 578.2) with expected isotopic distribution ratios.

3.4 XPS studies: Coordinative interaction between iridium center and N^C site in Ir-NHC-CTFs and homogeneous [IrCp*(N^C)Cl]Cl were systematically studied by XPS. To analyze how the electronic environments around the C and N atoms of N^C ligand and NHC-CTF changes upon iridium complex formation, XPS of N^C ligand and NHC-CTF were compared with their respective iridium complexes.

Initially, the XPS of homogeneous [IrCp*(N^C)Cl]Cl and N^C ligand were studied. The deconvoluted N-1s



Figure 4. XPS Ir 4f spectra of (a) Ir_{0.68}-NHC-CTF and (b) homogeneous [IrCp*(N^C)Cl]Cl.

spectrum of N^C ligand showed two peaks at 398.7 and 400.7 eV binding energy (Figure 3a); the peak at 398.7 eV corresponds to pyridinic nitrogen species and the peak at 400.7 eV corresponds to imidazolium nitrogen species.^{43, 44} The C-1s deconvolution peaks (Figure 2a) at 284.6 and 285.7 eV demonstrate that it has two kinds of carbon species corresponds to C-C/C-H and C-N carbon species, respectively.44 Upon complexation with iridium metal center, the pyridinic nitrogen's binding energy was shifted from 398.7 to 399.8 eV (Figure 3a vs 3b) and the intensity of C-N carbon species was decreased (Figure 2a vs 2b). This indicate that the electron density around C-N and pyridinic nitrogen were reduced. The diminution of electron density was attributed to the consequences of electron donation from pyridinic nitrogen and C-N carbene species (NCHN unit) to the iridium metal center. The behavior of pyridinic nitrogen's upon complexation with metal (i.e. the shift to higher binding energy) was previously reported in Pt incorporated CTF by Schuth and co-workers.¹⁵ Ir-4f XPS spectrum showed that the binding energy for $Ir-4f_{7/2}$ level was 62.0 eV (Figure 4b), which was 0.7 eV lower than the IrCl₃ (62.7 eV).⁴⁵ This indicates that the valence state of Ir in homogeneous [IrCp*(N^C)Cl]Cl was Ir(III) and the electron density around the iridium center was much higher than the simple IrCl₃. Higher electron density at the iridium metal center indicates that the N^C and Cp* ligands donate electron densities to the iridium cation.

Next, the iridium interaction with NHC-CTF support in $Ir_{0.68}$ -NHC-CTF was established. As expected, the deconvoluted N-1s spectrum of NHC-CTF showed the presence of triazine/ pyridine (398.1 eV) and imidazoli-

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um (400.8 eV) nitrogen species (Figure 3c).^{15, 43} However, a new peak at 399.8 eV was also observed (Figure 3c). Similarly, apart from C-C/C-H and C-N carbon species, a new peak at 288 eV was observed in the deconvoluted C-1s spectrum of NHC-CTF (Figure 2c). The formation of these additional species were attributed to the high polymerization temperature used in the synthesis of NHC-CTF; this behavior was often observed in the syn-8 thesis of numerous CTFs.^{9,10,15,41} Coordinative interaction 9 of the NHC-CTF with iridium metal center result the 10 following changes in the C-1s and N-1s spectra. The de-11 convoluted N-1s spectrum showed a decrease in the in-12 tensity of the peak at 398.1 eV and an increase in the 13 intensity of the peak at 399.8 eV (Figure 3c vs 3d), which 14 can also be observed from the raw data (black). This 15 indicates that a fraction of nitrogen's binding energies 16 was shifted from 398.7 to 399.7 eV, similar to the behav-17 ior of N-1s spectra of N^C ligand vs homogeneous 18 [IrCp*(N^C)Cl]Cl. The deconvoluted C-1s spectrum 19 showed that the intensity of C-N species (the peak at 20 285.7 eV) was decreased (Figure 2c vs 2d), analogues to 21 the C-1s spectra of N^C ligand vs homogeneous 22 [IrCp*(N^C)Cl]Cl. These features indicate an interaction 23 of pyridinic and carbene (NCHN) sites of NHC-CTF with 24 iridium metal center as similar as that of the interaction 25 of N^C ligand with iridium metal center in homogene-26 ous [IrCp*(N^C)Cl]Cl.

27 The Ir-4f spectrum of Ir-NHC-CTFs showed that the 28 binding energy of Ir- $4f_{7/2}$ was 62.0 eV, (Figure 4a and 29 Figure S8), suggesting that Ir-NHC-CTFs and homoge-30 neous [IrCp*(N^C)Cl]Cl have identical binding energy 31 values. All these results collectively confirm that the 32 formation and coordination environment Ir-NHC-CTFs 33 are similar to that of reference homogeneous 34 [IrCp*(N^C)Cl]Cl. 35

3.5 Catalytic Hydrogenation of CO₂ into Formate: The as-synthesized Ir-NHC-CTFs were used as catalysts for CO₂ hydrogenation. The hydrogenation is usually carried out in amine solutions to trap formic acid as formate-amine adduct.⁴⁶ Thus, using Ir-NHC-CTFs the hydrogenation was carried out in a 1.0 M aqueous triethylamine solution. Initially, the hydrogenation was performed using Ir_{0.68}-NHC-CTF catalyst at a stirring speed of 300 RPM. As shown in Table 1, entry 1, at 80 °C and under a total pressure of 4.0 MPa, Ir_{0.68}-NHC-CTF afforded a substantial TON of 800 within 2 h, which was nearly ~1.5 times higher than the previously reported bipyridine-based half-sandwich Ir complex (bpy-CTF-[IrCp*Cl]Cl)¹⁴ under similar reaction conditions. This indicates that the introduction of an electron donating NHC ligand can significantly improve the efficiency of CO₂ hydrogenation catalysts as hypothesized.

With this result in hand, the catalytic efficiency Ir_{0.68}-52 NHC-CTF was further studied under different reaction 53 conditions to obtain the maximal activity. Initially, the 54 hydrogenation was studied at temperatures up to 160 °C 55 at a total pressure of 4.0 MPa $(CO_2/H_2 = 1)$ for 2 h. The 56

Table 1: Catalytic Performances of Ir-NHC-CTFs under various reaction conditions^a

Entry	Т	Р	Time	TON ^c	TOF ^d
	(°C)	(MPa) ^b	(h)		(h ⁻¹)
1	80	4.0	2	800	400
2	100	4.0	2	2155	1077
3	120	4.0	2	4050	2025
4	160	4.0	2	8450	4225
5	160	6.0	2	11550	5775
6	160	8.0	2	17330	8665
7	120	8.0	0.25	4000	16000 ^e
8	120	8.0	2	9200	-
9	120	8.0	5	14220	-
10	120	8.0	10	19655	-
11	120	8.0	15	24300	-
12 ^f	120	8.0	2	9230	-
13 ^g	120	8.0	2	9190	-
14 ^h	120	8.0	2	9250	-
15 ⁱ	120	8.0	2	6100	-
16 ^j	120	8.0	2	4250	-
				.)	

^aReaction conditions: 10.0 mg of Ir_{0.68}-NHC-CTF was dispersed in 1.0 M aqueous Et₂N solution (30 mL) and stirred at a rate of 300 RPM (rotation per minute) under desired pressure and temperature. ⁶Total pressure at room temperature $[CO_2:H_2 (1:1)]$. "TON = mole of formate/mole of Ir. ^dTOF = TON per hour. ^eInitial TOF calculated from the initial part of the reaction (after 15 min). ^fRPM = 1000. ^gRPM = 2000. ^hRPM = 2750. ⁱIr_{2.1}-NHC-CTF. ^jIr, NHC-CTF.

results shown in entries 2-4 show that the TON gradually increases at higher temperatures and reaches a TON of 8450 at 160 °C. The effect of pressure was subsequently investigated at 160 °C for 2 h. When the total pressure was increased from 4.0 to 6.0 or 8.0 MPa, a linear increase in activity was observed (entries 4-6), and attained a TON of 17330 at a pressure of 8.0 MPa in 2 h. This increase in activity with respect to pressure indicates that the rate of reaction is proportional to the pressure of both H, and CO, gases; suggesting the hydrogenation follows a first order kinetics with respect to both H₂ and CO₂.

Finally, the hydrogenation was monitored at different time intervals (Table 1, entry 7-11 and Figure S5). Analyzing the initial part of the reaction (15 min), it was revealed that Ir_{0.68}-NHC-CTF has an initial TOF of 16000 h^{-1} at 120 °C under a total pressure of 8.0 MPa, which is the highest value reported to date for any



Figure 5. Recyclability of $Ir_{0.68}$ -NHC-CTF at 120 °C under 8.0 MPa total pressure.

heterogeneous catalytic system.⁴⁶⁻⁵⁶ As shown in Figure S9, the generation of formate was gradually increased with time and a formate concentration of 0.282 M with a highest ever TON of 24300 was obtained in 15 h. Figure S5 shows that the rate of formate generation was faster at an early stage of the reaction (ca 2 h) compared to the end stage of the reaction. The similar behavior was previously observed in the ruthenium (half-sandwich oxinato complexes) catalyzed CO, hydrogenation.⁵⁷ To examine this behavior, the catalysts after 1, 5 and 20 h of hydrogenation were analyzed by XPS. As shown in Figure S10, the Ir 4f binding energy of all the samples (1, 5 and 20 h samples) were same (Ir $4f_{7/2} = 62.4$ eV and $Ir_4f_{5/2} = 65.4 \text{ eV}$), indicating that the coordination environment of Ir species after 1, 5 and 20 h of hydrogenation remains same, and thus the slow rate at the end stage of the reaction does not related to the coordination environment of Ir species. As shown in Figure S10, compared to Ir_{0.68}-NHC-CTF, the binding energies were slightly increased by 0.4 eV, indicates a decrease in the electron density at the Ir atom; this behavior might be attributed to the chloride ligand substitution by the more electron-withdrawing ligand such as generated formate anions. Although, the exact reason for the slower rate of formate generation at the final part of the reaction is not clearly understood, we expect that it may be attributed to the more competitive backward reaction, i.e., the decomposition of formate back into CO₂ to H₂, which usually promoted by most of such CO₂ hydrogenation catalysts.^{29,33,58,59} In addition, it could be due to the changes in the properties of the reaction medium such as dipole moment, pH,33 and etc., which expected to have significant difference between the initial and end stage of the reaction.

Then, to examine the external mass transfer effects on the reaction rate, the hydrogenation was performed at various stirring speed. The result showed that effect of stirring speed on the reaction rate was negligible (entries 12-14); indicating that the reaction rate may not rely on the external mass diffusion limitations in the current reaction conditions. Finally, using $Ir_{2,1}$ -NHC-CTF and $Ir_{3,5}$ -NHC-CTF catalyst the hydrogenation was performed. As shown in entries 15-16, the catalysts demonstrated TONs of 6100 and 4250, respectively at 120 °C under 8.0 MPa total pressure in 2 h.

Before checking the recycling ability, the heterogeneous nature of Ir-NHC-CTF was investigated by filtration tests. To test this, the catalyst Ir_{0.68}-NHC-CTF was filtered after 1 and 5 h of hydrogenation and the resulting colorless filtrates were used as the catalytic solution. As shown in Figure S11, even after extended reaction time, no increment in the formate concentration was observed; indicates that the catalyst is purely working in a heterogeneous manner. Finally, to examine the recyclability of Ir_{0.68}-NHC-CTF, the black solid after the initial run was recovered by simple filtration and washed with water, dried, and directly used in the next run. As shown in Figure 5, the catalytic efficiency of Ir_{0.68}-NHC-CTF was slightly decreased in the successive runs and about 90% of the activity was retained in each recycles. XPS of the recovered catalyst (after 3 cycles) showed no subtle changes in the binding energies of Ir (Ir $4f_{7/2} = 62.4$ eV and $Ir_{4f_{5/2}} = 65.4 \text{ eV}$) compared to the binding energy of Ir after 2 h of initial run (Figure S10), suggesting that the coordination environment around the Ir metal center is retained. However, ICP-OES analysis of the filtrate (in each recycles) revealed that ca 6.4-7.2% of the loaded Ir has been leached. These results suggest that the reduced activity of Ir_{0.68}-NHC-CTF at the successive runs may be originated from the Ir leaching. The origin of Ir leaching into the solution is currently under investigation.

4. CONCLUSION

In conclusion, a novel covalent triazine frameworkfunctionalized with Ir-NHC complex (Ir-NHC-CTF) was synthesized using a solid chelating ligand containing NHC sites through post-synthetic immobilization technique. The coordination environment around the Ir(III) center in Ir-NHC-CTF was closer to the reference homogeneous [IrCp*(N^C)Cl]Cl. The strong σ -donating and poor π -accepting characters of NHC site in the CTF enhances the electron density on central metal Ir(III) cation. As a result, the Ir-NHC-CTF demonstrated an excellent activity towards the hydrogenation of CO2 to formate with TOFs of 16000 h⁻¹ and TONs of 24300, which are the highest values reported to date in heterogeneous catalytic systems. Thus, the result opens new opportunities for improving the efficiency of heterogeneous catalysts across various catalytic processes.

ASSOCIATED CONTENT

Supporting Information

Details of the synthetic procedures and analytical data of presented CTFs included. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

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A covalent triazine framework, functionalized with Ir-NHC sites, has demonstrated a highest ever TOF of 16,000 h^{-1} and TON of 24,300 for the hydrogenation of CO₂ to formate.

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